

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
11 April 2002 (11.04.2002)

PCT

(10) International Publication Number
WO 02/28986 A1

(51) International Patent Classification⁷: **C09K 21/12**

(21) International Application Number: **PCT/KR01/01634**

(22) International Filing Date:
28 September 2001 (28.09.2001)

(25) Filing Language: **Korean**

(26) Publication Language: **English**

(30) Priority Data:
2000/58436 5 October 2000 (05.10.2000) **KR**

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- entirely in electronic form (except for this front page) and available upon request from the International Bureau

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **ORGANIC PHOSPHORUS FLAME RETARDANT AND FLAME RETARDANT THERMOPLASTIC RESIN COMPOSITION CONTAINING THE SAME**

(57) Abstract: The present invention provides an organic phosphorus flame retardant prepared by coating organic phosphorus compound with an emulsifier and insulating the coated organic phosphorus compound with a thermosetting resin. The flame retardant resin composition containing the organic phosphorus flame retardant of the present invention shows a good physical properties including flame resistance.

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**ORGANIC PHOSPHORUS FLAME RETARDANT AND FLAME
RETARDANT THERMOPLASTIC RESIN COMPOSITION
CONTAINING THE SAME**

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Field of the Invention

The present invention relates to an organic phosphorous flame retardant. More particularly, the present invention relates to an organic phosphorous flame
10 retardant that is prepared by coating phosphorous compound with an emulsifier and by capsulation of the coated phosphorous compound with a thermosetting resin. Further, the present invention relates to a flame retardant thermoplastic resin composition containing the organic phosphorous flame retardant.

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Background of the Invention

Thermoplastic resins have been extensively utilized in a variety of applications such as electronic components and parts, electric articles, machines,
20 automobiles, office goods etc. As the thermoplastic resins require sufficient flame retardancy, various flame retardant agents are used in a large amount. Fire accidents can be prevented in advance by providing the thermoplastic resins with flame retardancy, and, once a fire has occurred, expansion of the fire can be prevented by minimizing occurrence of flame. For these purposes, the thermoplastic resins
25 contain various flame retardants such as halogen compounds, inorganic hydroxides, nitrogen compounds, phosphorous compounds etc.

The halogen compounds can provide the thermoplastic resins with a good flame retardancy and good mechanical properties. However, the thermoplastic resins liberate during the molding process toxic halogen gases that are harmful to the
30 molding apparatus. And the resins liberate during combustion dioxins that are

detrimental to human beings.

In case of use of an inorganic hydroxide, a large amount of the inorganic hydroxide should be used to give sufficient flame retardancy. The use of the large amount of an inorganic hydroxide results in a poor molding processability.

5 In case of use of a nitrogen compound as a flame retardant, the flame retardancy is not so good and toxic gases are liberated during combustion.

In case of use of a phosphorous compound as a flame retardant, the mechanical properties can be deteriorated. Preferred phosphorous compounds are organic phosphorous compounds such as triphenylphosphate (TPP), and red
10 phosphorus. U.S. Patent No. 4,879,067 to Sakon et al discloses a flame retardant that is prepared by coating red phosphorus with an inorganic hydroxide such as aluminum hydroxide and zinc hydroxide and coating the red phosphorus with a thermosetting resin. However, as the red phosphorus is vulnerable to heat, friction or impact, it is not easy to treat, handle, store and blend. Further, as the red phosphorus
15 reacts with oxygen in the air to produce toxic phosphine gas and oxidants, the working environment can be contaminated.

In case of use of a phosphorus compound as a flame retardant, there exist many difficulties. For example, in case of use of TPP as a flame retardant, the thermoplastic resin shows much difficulty during the molding process because the
20 TPP has a lower melting point of about 48 °C, and poor mechanical properties because the TPP forms bridges with the base resin during the molding process. In case of use of tricresylphosphate as a flame retardant, it is difficult to blend uniformly a powder or pellet form base resin and the flame retardant because tricresylphosphate is liquid at room temperature. The blending problem can cause
25 mechanical properties such as impact strength in the molded articles.

Korean Patent No. 68962 teaches a flame retardant that is prepared by immersing red phosphorus in polymethylmethacrylate (PMMA) polymer solution, and a flame retardant thermoplastic resin using the red phosphorus.

The present inventor has developed a capsulated organic phosphorous flame
30 retardant not adversely affecting the mechanical properties such as impact strength,

and a thermoplastic resin composition using the flame retardant so that the shortcomings of the conventional thermoplastic resin compositions might be overcome.

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Objects of the Invention

A feature of the present invention is the provision of a capsulated organic phosphorous flame retardant that can be used in a thermoplastic resin composition to provide good flame retardancy.

Another feature of the present invention is the provision of a method of preparing a capsulated organic phosphorous flame retardant which is prepared by coating phosphorus compound with an emulsifier and by capsulation of the coated phosphorus compound with a thermosetting resin.

A further feature of the present invention is the provision of a flame retardant thermoplastic resin composition with good mechanical properties such as impact strength at a high temperature during extrusion or injection.

A further feature of the present invention is the provision of a method of preparing a flame retardant thermoplastic resin composition using the capsulated organic phosphorous flame retardant.

Other objects and advantages of this invention will be apparent from the ensuing disclosure and appended claims.

Summary of the Invention

The capsulated organic phosphorous flame retardant according to the present invention is prepared by coating an organic phosphorous compound with an emulsifier and by capsulation of the coated phosphorous compound with a thermosetting resin. Preferred organic phosphorous compounds are TPP and

tricresylphosphate. Polyvinylalcohol can be preferably used as an emulsifier.

Preferred thermosetting resin is amino plastic such as melamine/formaldehyde resin and urea/formaldehyde resin.

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Detailed Description of the Invention

To prepare the capsulated organic phosphorous flame retardant according to the present invention, an organic phosphorous compound is coated with an
10 emulsifier, and the coated phosphorous compound is insulated with a thermosetting resin like a capsule.

Preferred organic phosphorous compounds usable in the present invention are phosphoric acid esters such as TPP and tricresylphosphate, but, not limited to these compounds. The organic phosphorous compound is coated with an emulsifier. The
15 phosphoric acid esters are a powder state or a liquid state at room temperature because the melting point is lower. TPP has a melting temperature of about 48 °C and is a powder state at room temperature, and tricresylphosphate is a liquid state at room temperature. The powder or liquid state phosphorous compound is dispersed in an emulsifier to prepare aqueous emulsion. Polyvinylalcohol can be preferably used
20 as an emulsifier. An aqueous solution of about 5 % by weight of polyvinylalcohol is preferably used. The emulsion of the organic phosphorous compound dispersed in the emulsifier has preferably an average particle size of about 3 to 10 µm. The organic phosphorous compound dispersed in the emulsifier forms particles coated with membrane of emulsifier. Thus, the phosphoric acid ester particles are coated
25 with polyvinylalcohol.

The phosphoric acid ester particles primarily coated with polyvinylalcohol is insulated with a thermosetting resin to form capsulated particles. Preferred thermosetting resin is amino plastic such as melamine/formaldehyde resin and urea/formaldehyde resin. As the amino plastic has flame retardancy in itself, a
30 synergic effect can be obtained when it is used with a phosphoric acid ester.

Melamine/formaldehyde resin is prepared by dissolving melamine in an aqueous solution of formaldehyde and sodium hydroxide. Aqueous solution of formaldehyde and aqueous solution of sodium hydroxide are mixed together and added with melamine during agitation at 70~80 °C. It is preferable to mix about 20
5 ~50 % by weight of aqueous solution of formaldehyde and about 10 ~30 % by weight of aqueous solution of sodium hydroxide. The molar ratio of melamine to formaldehyde is about 3 to 1 and it is preferable to produce methylolated melamine of about 2.5~3.5 equivalents. The methylolated melamine is added to the phosphoric acid ester emulsion in which phosphoric acid ester particles are primarily coated
10 with polyvinylalcohol. The resulting solution is agitated at 70~80 °C for 100~150 minutes to control pH at 5.0~6.0. The methylolated melamine forms melamine resin through condensation. Phosphoric acid ester particles primarily coated with polyvinylalcohol are capsulated with melamine/formaldehyde resin so as to prepare a flame retardant according to the present invention. The flame retardant comprises
15 an inner portion of organic phosphorous compound, a primary layer of polyvinylalcohol, and an outer capsulated membrane of melamine/formaldehyde resin.

The flame retardant solution after capsulation is filtered through a conventional method. Before filtration, unreacted formaldehyde is preferably
20 removed. The unreacted formaldehyde affects adversely mechanical properties of the molded articles. In particular, if the flame retardant is used more than 20 % by weight on the basis of the total resin composition, the molded articles show bubbles which are surely caused by the unreacted formaldehyde. Therefore, before filtration, the unreacted formaldehyde is preferably removed in emulsion state by adding
25 ammonia thereto.

After filtration, the liquid state capsulated phosphorous flame retardant is dried to a solid state or a powder state. The solid state flame retardant should be pulverized into a powder state. The powder state flame retardant is blended with a base resin to prepare a flame retardant thermoplastic resin.

30 In conventional methods to prepare a flame retardant thermoplastic resin

using an organic phosphorous flame retardant, much difficulty follows in the molding process because of the lower melting point of the organic phosphorous compound. As TPP has a melting point of 48 °C and tricresylphosphate is a liquid state, dispersity and compatibility become poor when they are blended with a base resin. However, the capsulated flame retardant according to the present invention does not deteriorate the compatibility as well as other mechanical properties because the organic phosphorous compound does not directly contact with the resin due to the insulated membrane formed with a thermosetting resin.

The capsulated flame retardant is used in an amount of about 10 to 30 % by weight as per 100 % by weight of the base resin. The base resin includes polystyrene, acrylonitrile/butadiene/styrene (ABS), ABS/polycarbonate alloy, polyamide, polyester, polyether, polycarbonate, polyacrylate etc.

The resin composition using the capsulated flame retardant according to the present invention shows good flame retardancy and impact strength compared to the conventional resin compositions not using the capsulated flame retardant.

Other additives may be contained in the resin composition of the present invention. The additives include an additional flame retardant, a lubricant, a releasing agent, an anti-dripping agent, an impact modifier, a plasticizer, a heat stabilizer, an oxidation inhibitor, a light stabilizer, a compatibilizer and the like. An inorganic filler such as talc, silica, mica, glass fiber, an organic or inorganic pigment and/or dye can be added too. The additives are employed in an amount of about 0 to 60 parts by weight as per 100 parts by weight of the flame retardant thermoplastic resin composition, preferably about 1 to 40 parts by weight.

The flame retardant thermoplastic resin composition according to the present invention can be prepared by a conventional method. All the components and additives are mixed together and extruded through an extruder and are prepared in the form of pellets.

The flame retardant thermoplastic resin composition according to the present invention can be applied to electric or electronic goods, automobile parts, office

supplies, etc which require good flame retardancy, weld-line strength and impact strength.

The invention may be better understood by reference to the following
5 examples which are intended for the purpose of illustration and are not to be construed as in any way limiting the scope of the present invention, which is defined in the claims appended hereto. In the following examples, all parts and percentage are by weight unless otherwise indicated.

10 **Examples 1A: Preparation of Capsulated TPP**

Polyvinylalcohol was used as an emulsifier. An aqueous solution of about 5 % by weight of polyvinylalcohol was preferably used. To the aqueous solution of 300 g was 200 g of TPP added to prepare an aqueous emulsion. The emulsion of the
15 organic phosphorous compound dispersed in the emulsifier had an average particle size of about 5 to 6 μm . To 75 g of 37 % formalin was 20 % sodium hydroxide added, and 30 g of melamine was added at 75 °C during agitation. The methylolated melamine had about 2.5~3.5 equivalents. The methylolated melamine was added to the phosphoric acid ester emulsion in which phosphoric acid ester particles were
20 primarily coated with polyvinylalcohol. The resulting solution was agitated at 75 °C for 120 minutes to control pH at 5.2. The flame retardant solution after capsulation was filtered through a conventional method. Before filtration, unreacted formaldehyde was preferably removed. Before filtration, the unreacted formaldehyde was preferably removed in emulsion state by adding ammonia thereto.
25 After filtration, the liquid state capsulated phosphorous flame retardant was dried to a solid state or a powder state. The solid state flame retardant was pulverized into a powder state.

Examples 1B: Preparation of Capsulated Tricresylphosphate

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Capsulated tricresylphosphate was prepared in the same manner as in Example 1A except that tricresylphosphate was used instead of TPP.

Examples 2A-2C: Preparation of Thermoplastic Resins

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10, 20 and 30 parts by weight of the capsulated TPP of Example 1A as per 100 parts by weight of the base resin of ABS were used to prepare flame retardant thermoplastic resin compositions of Examples 2A, 2B and 2C, respectively.

Examples 3A-3C: Preparation of Thermoplastic Resins

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10, 20 and 30 parts by weight of the capsulated tricresylphosphate of Example 1B as per 100 parts by weight of the base resin of ABS were used to prepare flame retardant thermoplastic resin compositions of Examples 3A, 3B and 3C, respectively.

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Comparative Examples 1A-1C: Preparation of Thermoplastic Resins

10, 20 and 30 parts by weight of conventional uncapsulated TPP as per 100 parts by weight of the base resin of ABS were used to prepare flame retardant thermoplastic resin compositions of Comparative Examples 1A, 1B and 1C, respectively.

20

Comparative Examples 2A-2C: Preparation of Thermoplastic Resins

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10, 20 and 30 parts by weight of conventional uncapsulated tricresylphosphate as per 100 parts by weight of the base resin of ABS were used to prepare flame retardant thermoplastic resin compositions of Comparative Examples 2A, 2B and 2C, respectively.

30

Preparation of Test Specimens and Measurement of Mechanical Properties

The test specimens of the Examples and Comparative Examples were prepared with a twin axis extruder 30 mm (L/D is 30 : 1) at 200 to 250 °C. Izod impact strength (1/8") was measured for the specimens of Examples 2A-2C and 3A-3C in accordance with ASTM D256. The flame retardancy was measured in accordance with UL94VB. For each Example and Comparative Example, five specimens were tested for combustion time and average combustion time. The test results are shown in Tables 1 and 2.

Table 1

| Examples | Impact Strength | Flame Retardancy |
|----------|-----------------|------------------|
| 2A | 35 | V2 |
| 2B | 31 | V0 |
| 2C | 26 | V0 |
| 3A | 34 | V2 |
| 3B | 30 | V0 |
| 3C | 27 | V0 |

Table 2

| Comparative Examples | Impact Strength | Flame Retardancy |
|----------------------|-----------------|------------------|
| 1A | 14 | V2 |
| 1B | 10 | V0 |
| 1C | 4 | V0 |
| 2A | 15 | V2 |
| 2B | 9 | V0 |
| 2C | 5 | V0 |

As shown in Tables 1 and 2, the flame retardancy of the Examples is almost same as that of the Comparative Examples. However, the impact strength of the Examples is superior to that of the Comparative Examples.

- 5 The present invention can be easily carried out by an ordinary skilled person in the art. Many modifications and changes may be deemed to be with the scope of the present invention as defined in the following claims.

What is claimed is:

1. A method of preparing a capsulated organic phosphorous flame retardant,
which comprises:
 - 5 coating an organic phosphorous compound with an emulsifier; and
capsulating of the coated phosphorous compound with a thermosetting resin.
2. The method as defined in claim 1, wherein said organic phosphorous
compound is triphenylphosphate or tricresylphosphate.
- 10 3. The method as defined in claim 1, wherein said emulsifier is
polyvinylalcohol.
4. The method as defined in claim 1, wherein said thermosetting resin is amino
15 plastic.
5. The method as defined in claim 1, wherein said amino plastic is
melamine/formaldehyde resin or urea/formaldehyde resin.
- 20 6. The method as defined in claim 5, wherein the molar ratio of melamine to
formaldehyde is about 3 to 1 to produce methylolated melamine of about 2.5~3.5
equivalents.
7. The method as defined in claim 1, further comprising:
 - 25 filtering said phosphorous compound capsulated with a thermosetting resin;
and
drying the phosphorous compound to produce in a powder form.
8. The method as defined in claim 1, further comprising:
 - 30 removing unreacted formaldehyde from the phosphorous compound by adding

ammonia before filtering said phosphorous compound.

9. The organic phosphorous retardant prepared by the method of any one claim of claims 1-8.

5

10. A flame retardant thermoplastic resin composition comprising:
1-3 parts by weight of the organic phosphorous retardant prepared by the method of any one claim of claims 1-8; and
100 parts by weight of a base resin.

10

11. The flame retardant thermoplastic resin composition as defined in claim 10, wherein said base resin is selected from the group consisting of polystyrene, acrylonitrile/butadiene/styrene (ABS), ABS/polycarbonate alloy, polyamide, polyester, polyether, polycarbonate and polyacrylate.

15

12. The flame retardant thermoplastic resin composition as defined in claim 10, further comprising an additional flame retardant, a lubricant, a releasing agent, an anti-dripping agent, an impact modifier, a plasticizer, a heat stabilizer, an oxidation inhibitor, a light stabilizer and/or a compatibilizer.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR01/01634**A. CLASSIFICATION OF SUBJECT MATTER**

IPC7 C09K 21/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C08K5/49, 5/5333, C08L59/00, C08J5/00, C09K21/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Patents and applications for inventions since 1975

Korean Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NPS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| Y A | JP 07-53876 A2 (ASAHI CHEM. IND. CO. LTD) 28. FEBRUARY 1995 see the whole document | 1,2 10,11 |
| Y (| JP62-4746 A2 (TOEDTENANN GERT REINKING KLAUS) 10. JANUARY 1987 see claim 1-2, page2 column 2 line 20 - column 4 line 4 | 1 |
| A | EP 363,608 A1 (GENERAL ELECTRIC CO.) 18. APRIL 1990 | 10,11 |
| A | JP 07-278318 A (ASAHI CHEM. IND. CO. LTD) 24. OCTOBER 1995 | 10,11 |

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

31 JANUARY 2002 (31.01.2002)

Date of mailing of the international search report

31 JANUARY 2002 (31.01.2002)

Name and mailing address of the ISA/KR

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Facsimile No. 82-42-472-7140

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR01/01634

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| JP 07-053876 A2 | 28. 02. 1995 | FI 940464 A0 | 01.02.1994 |
| | | WO 9403535 A1 | 17.02.1994 |
| | | EP 611798 A1 | 24.08.1994 |
| | | DE 69321704 C0 | 26.11.1998 |
| | | US 5455292 A | 03.10.1995 |
| | | CN 1082074 A | 16.02.1994 |
| | | KR 163445 B1 | 15.01.1999 |
| JP 62-4746 A2 | 10. 01. 1987 | US 5234979 A | 10.08.1993 |
| | | EP 207359 A2 | 07.01.1987 |
| | | DE 3523316 A1 | 02.01.1987 |
| EP 363608 A1 | 18. 04. 1990 | AU 4334989 A1 | 18.04.1990 |
| | | US 5204394 A | 20.04.1993 |
| | | BR 8907094 A | 08.01.1991 |
| | | JP 2115262 A2 | 27.04.1990 |
| | | NL 8802346 A | 17.04.1990 |
| | | WO 9003417 A1 | 05.04.1990 |
| | | ES 2061834 T3 | 16.12.1994 |
| | | DE 68912700 C0 | 10.03.1994 |
| JP 07-278318 A | 24. 10. 1995 | KR 9305826 B1 | 25.06.1993 |
| | | None | |

